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ADVANCES IN SOLVENT-DEWAXING OF MINERAL OILS AND TARS

By Dr. Karl A. Fischer

A R T I C L E VII

NEW ELECTRO-OPTICAL ANALYSIS FOR PARAFFIN

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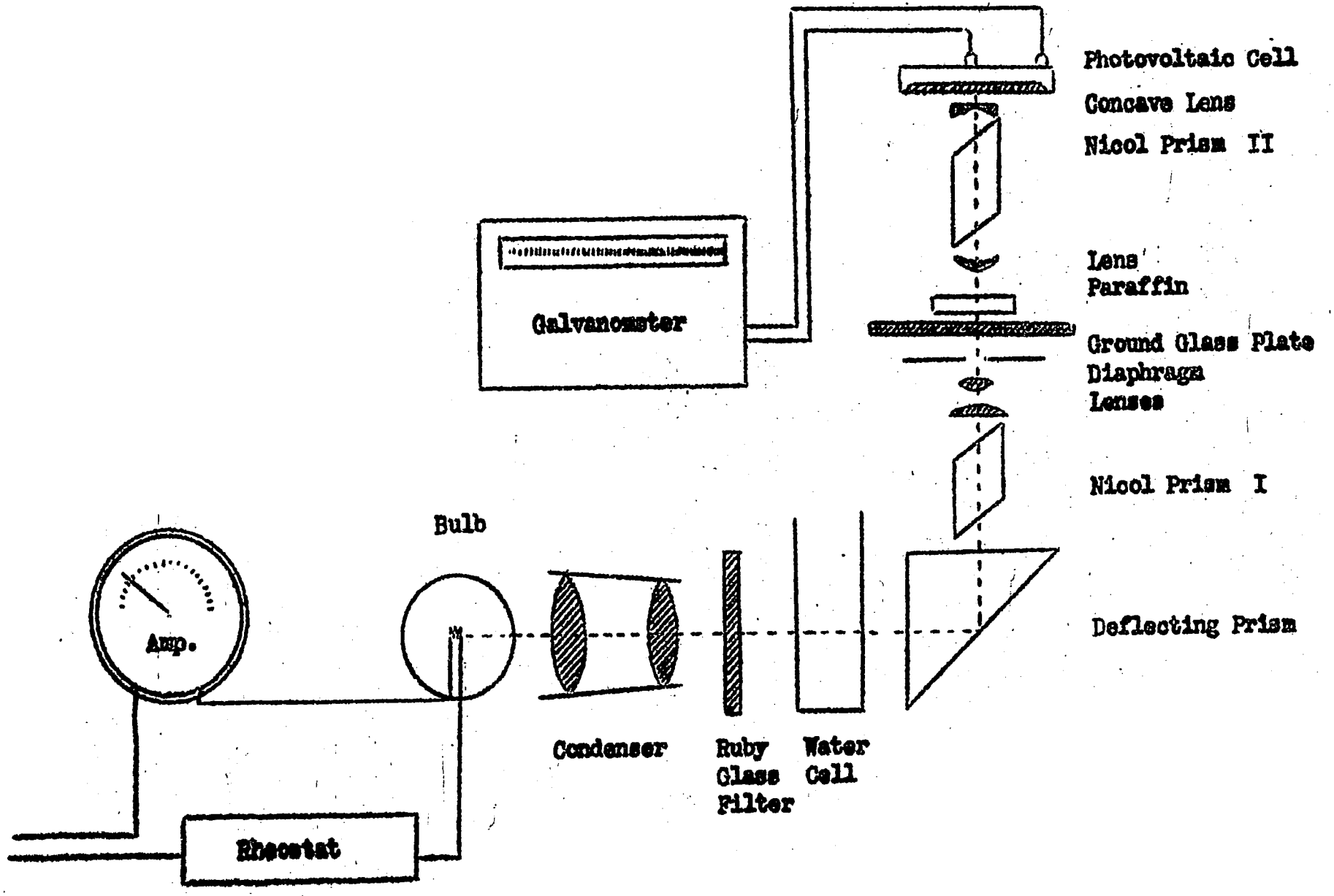
Analytical Determination of "Paraffin Wax" in Mineral Oils and Wax Cakes by a New Electro-Optical Method.

The usual method for the determination of paraffin wax in mineral oils and wax cakes requires the dilution of a weighed portion of the wax scales with various solvents. The solution must then be chilled to approximately -20°C, filtered and either the residue or the filtrate must be weighed after the removal of the solvent. Due to the solubility of paraffin wax in oil and solvent even at low temperature, conditions must be met carefully and the procedure is tedious and time consuming. In laboratory practice and especially in plant control work, immediate results are desired. The method described below will provide quick results (10 minutes) while the standard tests may be carried out simultaneously for checking and reference.

The new method eliminates dilution with solvents and is based on the principle that paraffin wax is doubly refracting when it is solid. Oil and molten wax as well as dissolved wax, on the contrary, are optically isotropic. Different paraffin waxes differ only slightly in optical activity. It is apparent that conditions can be created such as to give a measurable optical activity of wax oil mixtures which is proportional to the paraffin content.

Optical Arrangement. Light rays with large wave length have best penetrability through a turbid medium. It is therefore obviously advantageous to use red light which furthermore eliminates disturbance which might arise from fluorescence. The application of infrared light


Photovoltaic Cell
Concave Lens
Nicol Prism II
Galvanometer
Lens
Paraffin
Ground Glass Plate
Diaphragm
Lenses
Nicol Prism I
Bulb
Amp.
Deflecting Prism
Condenser
Ruby Glass Filter
Water Cell
Rheostat

did not bring any advantage, and even causes difficulties for reason of its heating effect and because more delicate and complicated assemblies are required.

The beam of light is supplied by a low voltage bulb, 30 Watts, which is connected with a well stabilized voltage outlet. It is filtered through a ruby glass filter, freed from heat rays by a water chamber and focused on a nicol prism. It then penetrates a fine ground glass plate and a thin layer of the sample to be examined and passes through a second nicol prism, which may be set parallel or crossed to the first one. An assembly of lenses and diaphragms insures that a uniform light beam of approximately 3 - 5 mm Ø is maintained throughout.

Electric Equipment. The light beam is directed to a photoelectric or photovoltaic cell. Cesium cells with amplifier and milliammeter or recorder give good results. A much simpler and cheaper apparatus, consisting of a photovoltaic cell (such as used in exposure meters) in connection with a sensitive galvanometer with taut suspended coil and mirror deflection proved just as satisfactory. In this case it is advantageous to use a diverging lens to spread the light beam over a larger surface of the cell, which gives better proportionality of light intensity to electromotoric force.

Procedure. It is evident that the required proportionality can only be obtained if the sample to be tested has a most exactly defined thickness, which can also be accurately reproduced with certainty. The wax should crystallize in a multitude of tiny crystals, arranged in all conceivable positions, such as to give mean optical activity. Double refractivity is naturally different for various crystalline axes and a preferred and directed growth of crystals is to be avoided. The thickness of the waxy layer must not exceed the limit which for high

paraffin percentages gives maximum transmission of light between crossed nicols. A thicker film will not allow more light to pass, but frustrates high % readings. The influence of turbidity becomes predominant in thicker paraffinic layers. It spoils proportionality of double refractivity to wax content.

The required conditions can be easily created by transferring a drop of the molten wax scales to a counting chamber for blood corpuscles, such as it is used by physicians. The chamber is then heated to 80-100°C and let cool down at room temperature. Thus correct film thickness of exactly 0.100 mm is obtained. Frequent tests have proved that the mean double-refractivity of standard wax - oil mixtures was well within the limits of error of paraffin determinations by conventional methods, although the average size of the wax crystals may have varied for the different preparations. That fact is visible, because different crystal size causes different turbidity of the preparation. It does not matter, however, because that variable is completly eliminated mathematically, as it will be seen later.

Testing. The paraffin sample to be examined is melted. For wax content above 60 - 70% it is advisable to dilute the sample with an equal amount of dewaxed oil. No other preparations are needed, unless the wax cake contains solvent, which must be evaporated on a watch glass. For low wax content (below 25%) it will be necessary to apply a thicker film. Specially ground chambers, or the use of two commercial chambers which give 0.200 mm film thickness may be used.

One drop of the test sample is placed on the slightly heated counting chamber. The chamber is then covered with a thick plane - parallel glass plate which is fixed with two clips. The preparation is heated

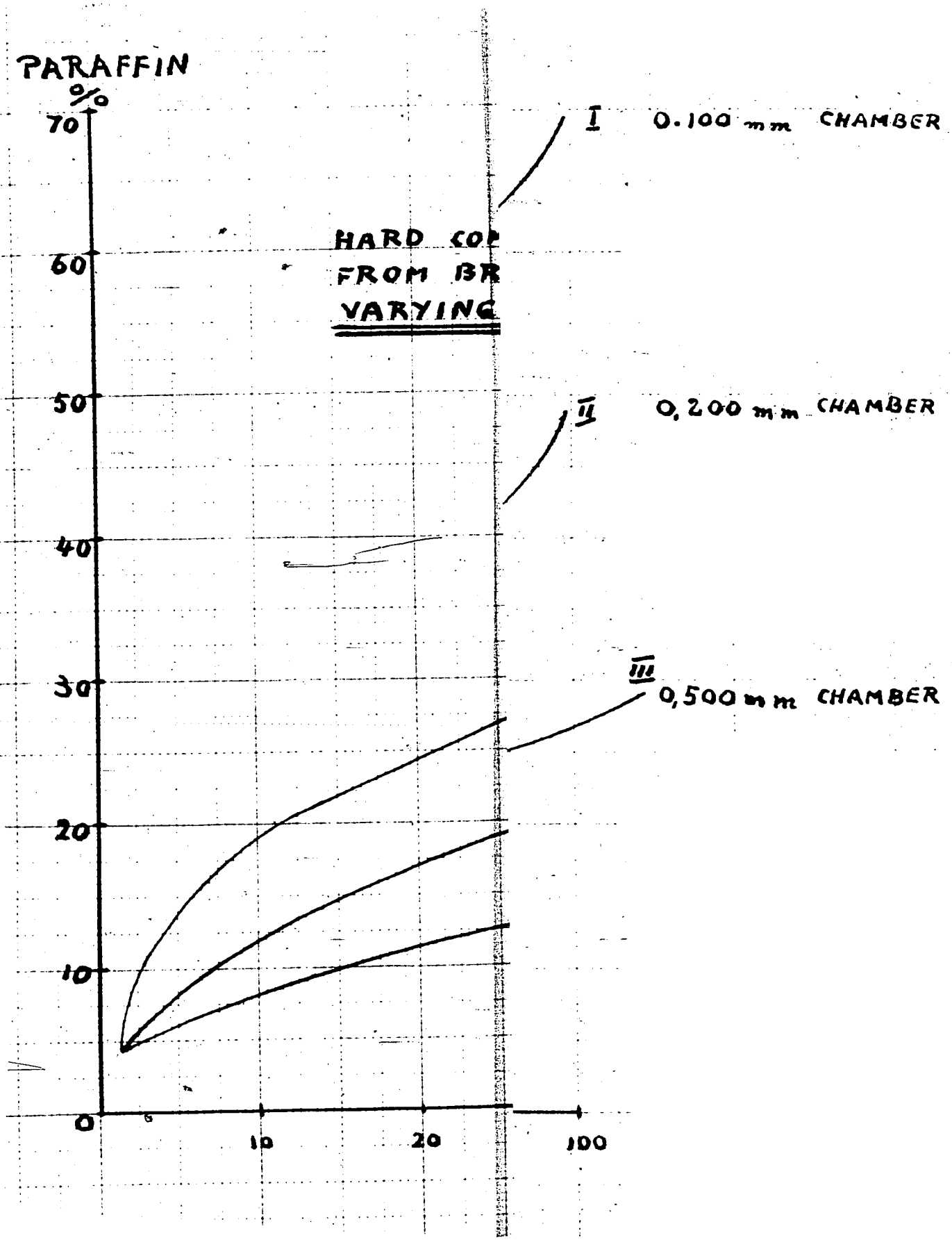
to 80 - 90°C in an oven, left standing at room temperature until the wax solidifies and finally immersed into water of 20°C. The chamber is taken out after 5 minutes, adhering water is dabbed off with filter paper and the sample is ready to be examined.

It is placed between the nicols of the apparatus and two readings are taken, one between parallel nicols and another between crossed nicols. It is advantageous if the galvanometer has a scale division of 100 parts and if its sensitivity can be varied by a variable shunt. Light intensity or the shunt will be adjusted such as to give maximum deflection between parallel nicols, but the reading need not be precisely 100. This reading gives the standard for light penetration through the sample, and the adjustment must be done individually for every sample depending upon turbidity, oil content and size of wax crystals. This may be called reading "A".

A second reading is then taken between crossed nicols which will obviously give a lower figure, because only a part of the light, proportional to the paraffin content of the sample, reaches the photoelectric cell. Reading "B".

It is now evident that the turbidity of the preparation is completely eliminated if the quotient of the two readings is taken, because the relation $\frac{B}{A} \cdot 100$ is constant. Regardless of what the reading "A" may have been it tells the quantity of light, which passes the preparation due to polarization in reference to the maximum light quantity which could pass the paraffinic layer if the optical activity was 100%. (Expressed by reading between parallel nicols).

Valuation. Standard preparations are made from oil free wax and dewaxed oil and are blended such as to give 10%, 20%, 30% etc. of


PARAFFIN
%
70
60
50
40
30
20
10
0
10
20
100
HARD COP
FROM BR
VARYING
I 0.100 mm CHAMBER
II 0,200 mm CHAMBER
III 0,500 mm CHAMBER

PARAFFIN %

HARD COMMERCIAL PARAFFIN FROM BROWN COAL TAR WITH VARYING CONTENT OF TAR OILS

I 0.100 mm CHAMBER

II 0,200 mm CHAMBER

III 0,500 mm CHAMBER

70
60
50
40
30
20
10
0

10 20 30 40 50 60 70 80 90 100

$$Q = \frac{\text{POLARIZATION}}{\text{PERMEABILITY}} = \frac{B}{A} \cdot 100$$

wax content. These preparations are submitted to the above described analytical procedure. The obtained quotients are then plotted against paraffin content. (See graph) Unknown samples can then be tested as it has been described above and the result is taken from the graph.

Example: Reading "A" = 50 $\frac{B}{A} \cdot 100 = 80$, wax % = 54%

" "B" = 40

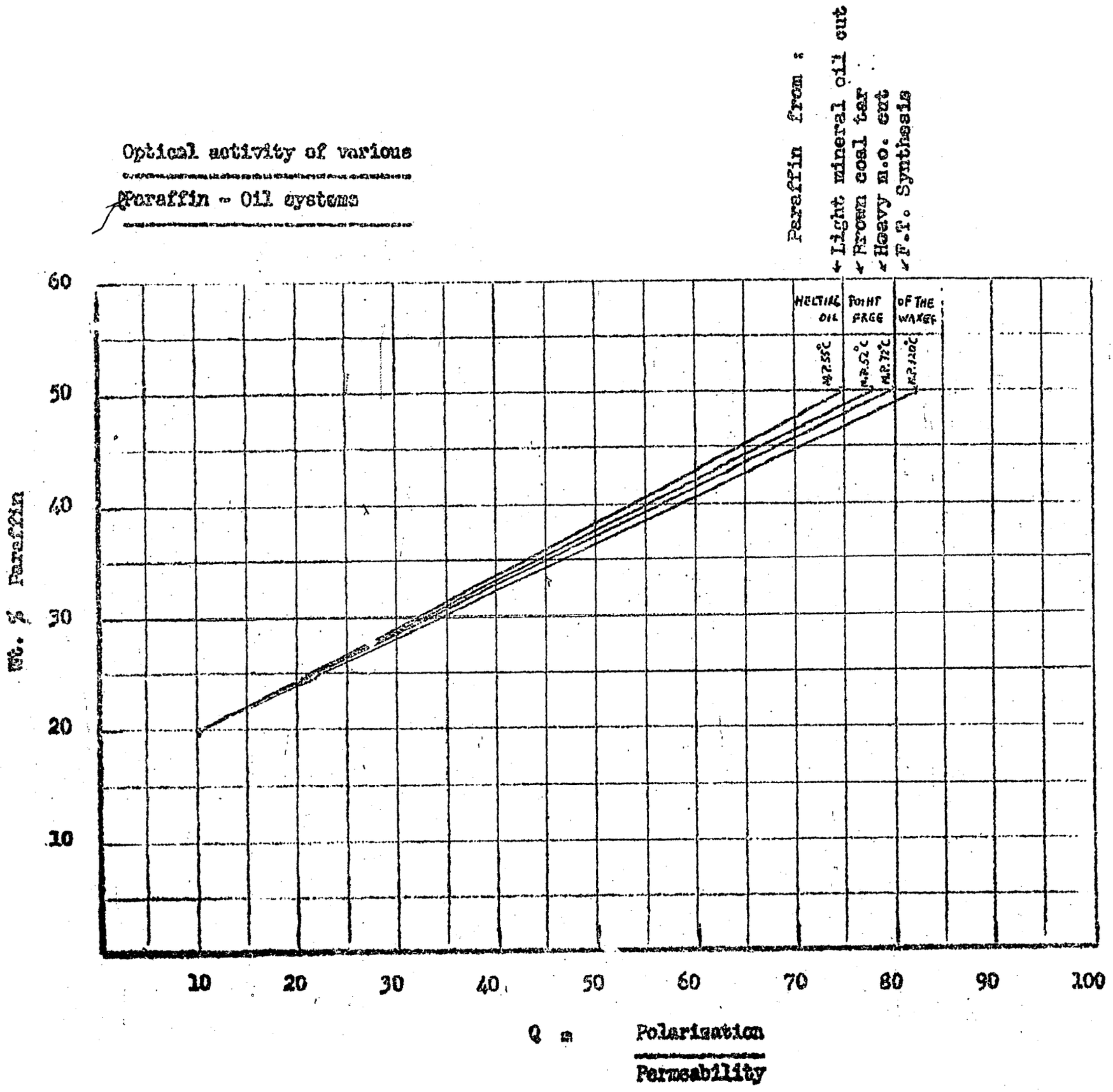
The curve is a straight line for wax percentages 25%-65%. The paraffin content can be read from the graph for any unknown oil wax mixture as soon as the quotient has been determined and the analysis takes but a few minutes and requires very little material. Obviously only the wax which is solid at observation temperature is measured. The mean value of several readings shall be taken.

Remarks. The curve runs steep for low wax percentages and extremely steep for high ones. The method can be adapted to those cases by diluting high percentage waxes with wax free oil and by examing the samples which are poor in wax content in thicker layers. It is to be considered, however, that the solubility of wax in oil, which is negligible for average concentrations, cannot be neglected for low wax percentage. It is then advisable to chill the preparation in ice water, tempering it to $0^{\circ}C$ instead of $20^{\circ}C$ and to plot a new curve for those conditions. Examination must then be done quickly to prevent the chamber from warming up. This is particularly essential for samples which contain low melting paraffins.

Chilling the test sample to temperature below $0^{\circ}C$ requires special protective measures and serious errors can result from frozen water, which also is doubly refracting. Wetting the slides with glycerin or alcohol may help eventually.

Optical activity of various

Paraffin - Oil systems



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It has been said above that there are slight differences in the optical activity of different paraffins. (See graph). For reliable results it is therefore necessary to plot the quotient curve for the wax which is to be tested later. It is a small job only to produce some oil free wax from the concerned product and to purify the paraffin by repeated precipitation from its solution in any of the well known solvents.

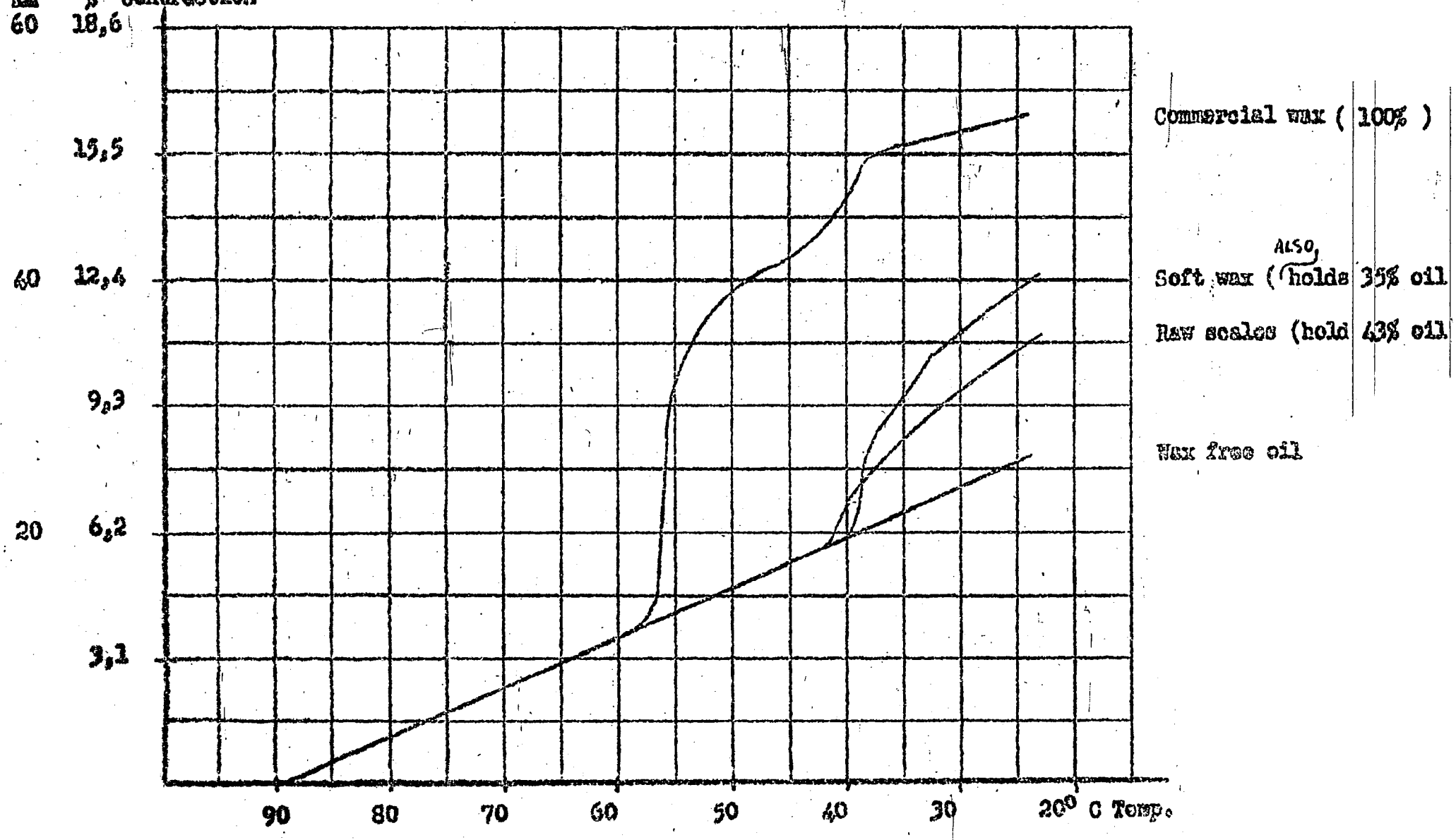
Discussion. It is advisable to check the results by preparing several chambers with the same test object. The results are usually within the same limits of error as the conventional precipitaion methods.

However, in a few cases, and among many correct results there happens a reading which is decidely wrong. The reason for that could not be found with certainty. The formation of a different crystal modification with different optical activity might be to blame for it. There is no doubt that paraffin wax occurs in different modifications when solid. If contraction or density is plotted against temperature there are several bends in the curve. The following curve shows that behaviour. (See next page) On the other side it is apparent that not much happens at 20°C, at least nothing which is reflected in a pronounced leap in gravity or volume. But the presence of oil may conceal crystalline changes to a certain extent and no satisfactory answer can therefore be given as yet.

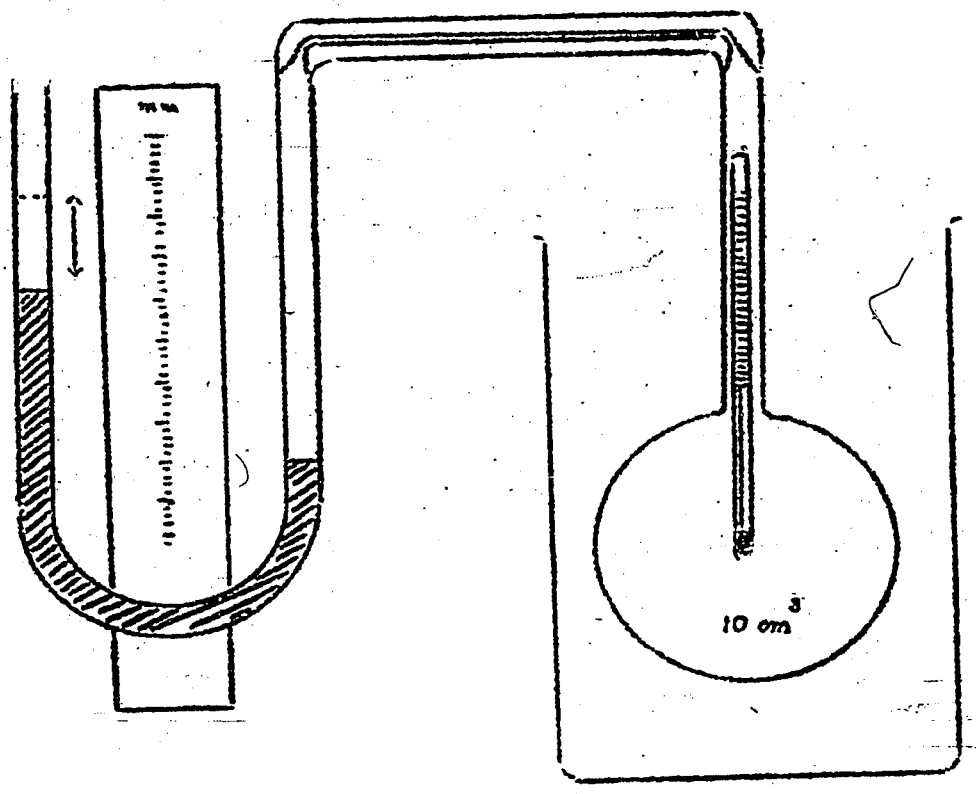
It is interesting to see that no correct calculation of the density of solid paraffins at a given temperature is possible from the density of wax which was measured at any other temperature. This was known for the calculation of the spec. gravity of solid paraffin from molten wax, but the calculation gives unreliable results also if the solid phase is considered exclusively. This behaviour naturally also reflects in wax bearing oils, though the error may then be negligible. No irregularities

Contraction Curve Of Brown Coal Tar Paraffin

Flask holds 10 cm^3 of paraffin. 1 mm contraction = 31 mm^3



Contraction of Paraffin



were observed or could be anticipated in the gravity-temperature curve of molten paraffin. Gravity of molten paraffin can therefore be calculated from the spec. grav. of molten wax at another temperature and is a reliable basis for analytical methods such as in the determination of the molecular weight with Eötvös's rule.

The penetration of light through various wax samples between parallel and crossed nicols was recorded in many tests. The result was always that comparable curves checked well and that nothing seemed to happen after 5 - 10 minutes time at room temperature. (See graph) One centimeter of the ordinate is equivalent to 5 minutes. The left curve gives the light intensity between crossed nicols, the right one records the turbidity, which is proportional to the light intensity between parallel nicols. The graphs also show that the two curves do not interfere up to 70% paraffin content. For higher percentages of wax there is an interference of both curves and the influence of turbidity becomes predominant. It is to be considered that the left curve records on its abscissa the light transmission for reason of double refractivity minus light absorption by turbidity. The right curve gives light absorption by turbidity only.

The complex nature of a solidifying highly waxy preparation becomes also evident, if we study dependence of light penetration between crossed nicols upon cooling velocity. While the curve for lower chilling rates is almost hyperbolic, there is a curve of higher order obtained in quick chilling. It is obvious that in both cases the growth of crystals will be much different and that the slope of the turbidity curve and of the curve of optical activity will interfere in many points. There are two amazing facts, however. 1) In both ways the

Transmission of light through 0,100 mm of solidifying paraffin

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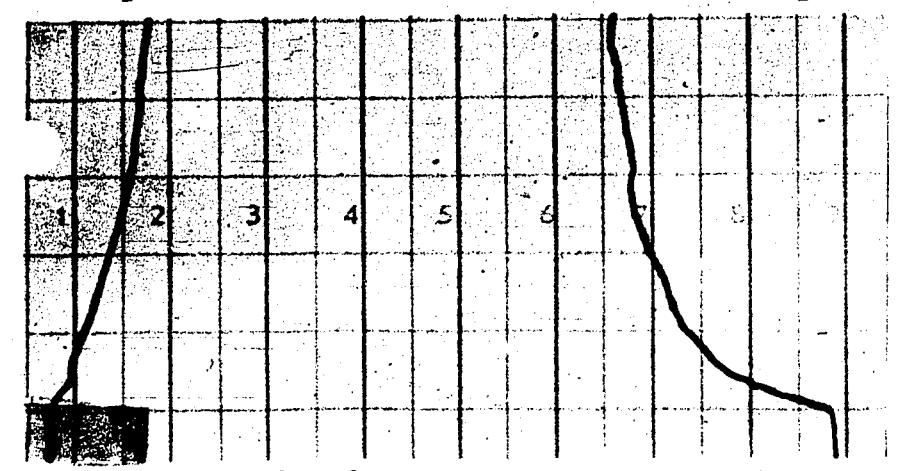
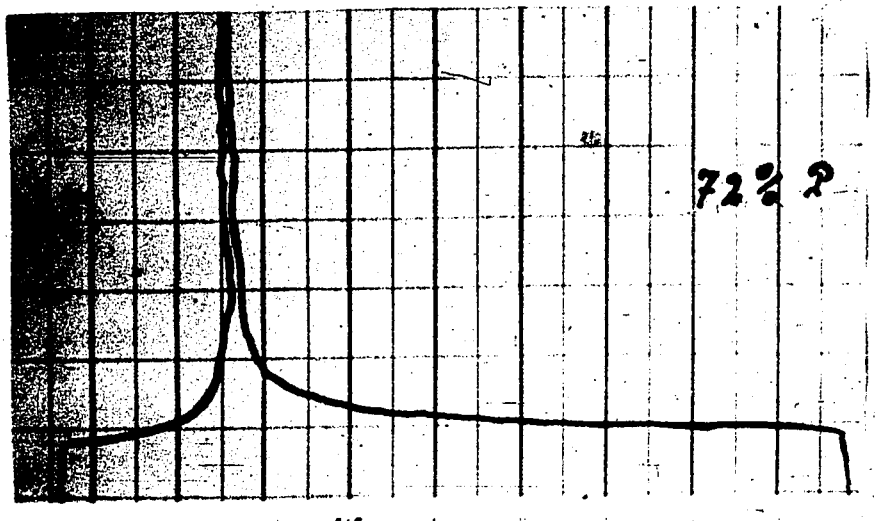
crossed Nicol prisms **parallel Nicol prisms**



23% paraffin
77% oil

53% paraffin
47% oil

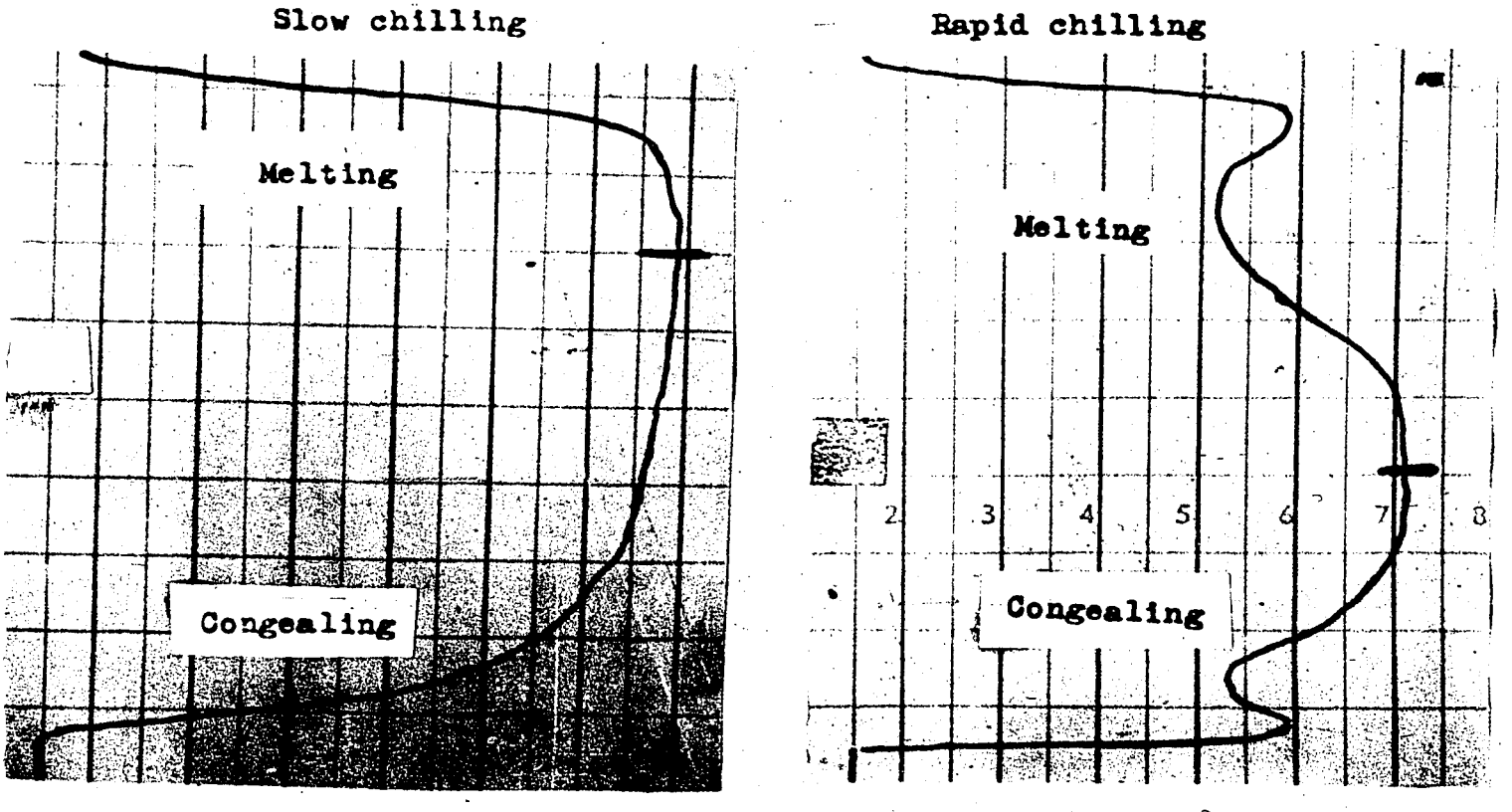


72% paraffin
28% oil

100% paraffin
0% oil

same reading is obtained as the final result regardless of what has happened during crystallization. 2) In melting the sample the reverse curve of the solidifying process is obtained, reflecting exactly whether the preparation had been chilled quickly or slowly. There is only one conclusion possible, that even varying number of crystals and their arrangement in space give a constant mean double refractivity within

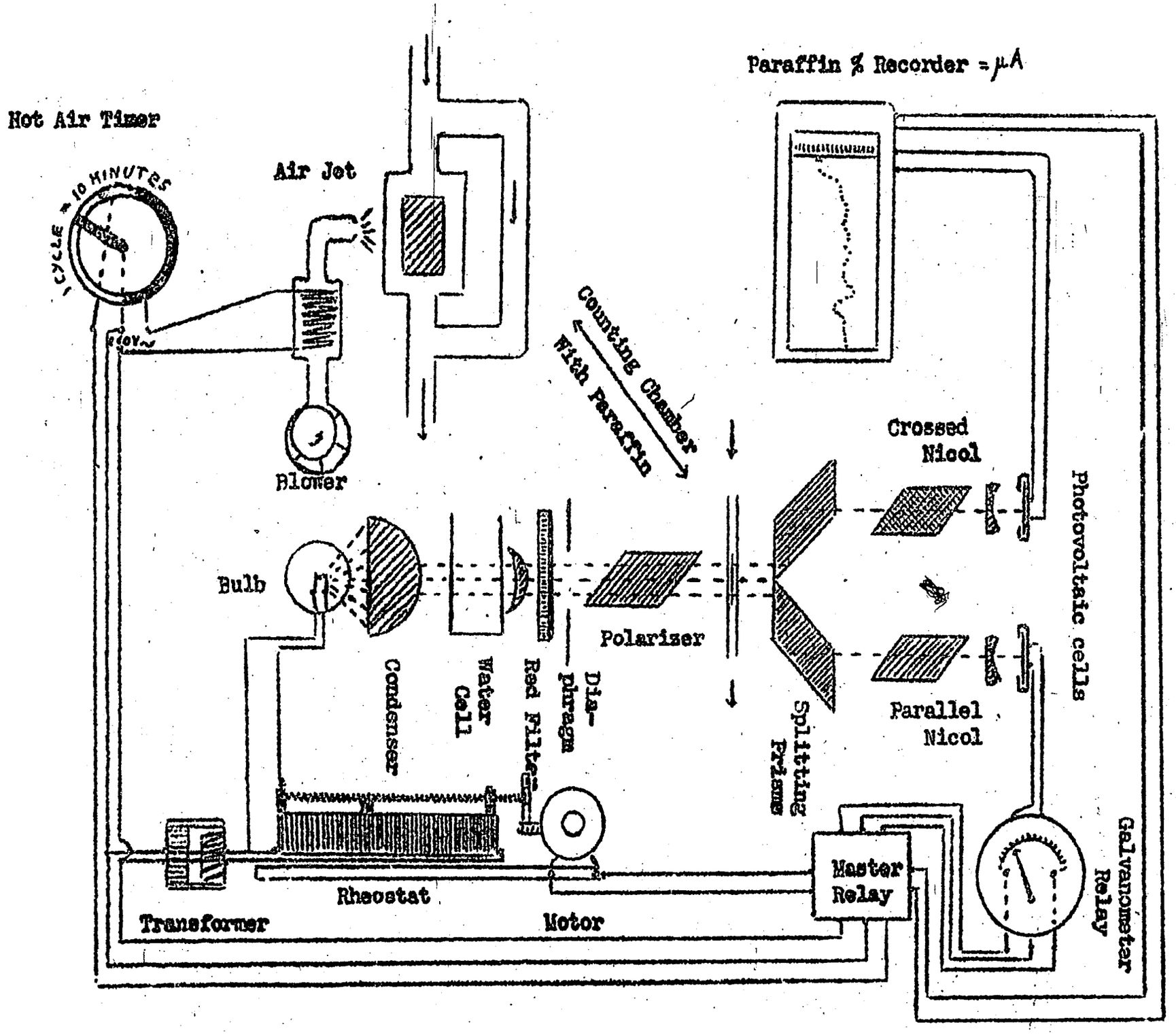
Curves of transmission of polarized light through 0,100 mm of paraffin



wide limits of chilling rate, which just proves that the above described method which measure mean final optical activity is applicable,

Wax Recorder. Instruments, which continuously record paraffin percentage of wax cakes on a purely physical principle, do not exist on the market. Such an instrument will be highly desirable for plant control and I therefore tried to use the discussed principle of electro-optical analysis in the design of a recording instrument. It is evident that light transmission through a paraffin layer of given thickness between crossed nicols will be proportional to wax content, if the influence of turbidity can be eliminated. It follows from the Quotient $\frac{B}{A} \cdot 100$, that wax % is proportional to reading B if the galvanometer deflection A is made 100 scale divisions for any paraffin sample. This can be done by changing the sensitivity of the galvanometer with shunts or much better by varying intensity of the light source with a rheostat. The optical, electric and purely mechanic assembly does not offer problems which are difficult to solve, but the continuous preparation of well defined paraffin layers, is not easy to produce. The demand to have a defined layer of exactly 0.100 mm thickness, sandwiched between two glasses was answered by inserting a counting chamber for blood corpuscles into a continuous stream of the wax to be tested. The sketch on next page will make plain the design of the instrument.

A counting chamber is cemented between glass tubes in such a way that molten paraffin can flow through it. A much larger amount of molten wax will flow through a bypass. Tubes, with exception of the counting chamber, are fitted with a heating jacket. A nozzle is close to the chamber and can blow a jet of either hot or cold air towards it.


Paraffin % Recorder = μA
Hot Air Timer
1 CYCLE = 10 MINUTES
Air Jet
Blower
Counting Chamber
With Paraffin
Crossed Nicol
Photovoltaic cells
Bulb
Condenser
Water Cell
Red Filter
Dia-phragm
Polarizer
Splitting Prisms
Parallel Nicol
Galvanometer Relay
Master Relay
Rheostat
Transformer
Motor

The cold jet will cause the paraffin to solidify in the chamber and make it ready for examination with transmitted polarized light, while the hot jet will melt the preparation and open the path for fresh paraffin to flow throguh until the cold jet obstructs the chamber again and offers the analyzing light beam a new sample.

The instrument consists of one half circular contact bar on which a contact brush sweeps around one full circle in 10 minutes. The contact bar intermittently actuates the heater of the hot air jet for a few minutes, which melts the wax in the chamber. The heater is then out of commission during 5 - 7 minutes, which causes the wax to solidify under the influence of the cold air jet. Towards the end of the cold jet period another contact is closed, which causes a small motor to slowly run a slider along the windings of a rheostat, which increases voltage and makes the incandescent lamp (6 V, 5 A) shine with increasing brightness. The light from the bulb is directed parallel by condensing lenses, cooled by a water chamber and passes a ruby filter, a nicol prism and the wax chamber. The beam is then split in two by prisms. One beam goes through a nicol prism in parallel position and hits a photovoltaic barrier layer type cell (I), whereas the second beam passes another nicol in crossed position and then hits upon a second photovoltaic cell (II). Cell (I) actuates a galvanometer relay. Light intensity increases continuously until the relay pointer hits on a contact. That deflection shall be exactly equivalent to the 100 scale part deflection of a depressor bar recorder, which is worked by photovoltaic cell (II). For this adjustment the nicol of the cell (II) beam must be set parallel. The adjustment having been made it is permanently crossed again for taking the wax percent readings. Contact of the galvanometer relay

causes the depressor bar to print a dot on the recording sheet. By way of relays it reverses the current of the motor which moves the slider of the rheostat back to zero position, reversing the current again and switching it off. The hot air timer then heats the wax chamber, new wax enters the cell, is solidified by the cold air jet and the electro-optical assembly is set in motion at the end of the cooling period such as it has been described above. The necessary individual relays, electronic and ordinary, are advantageously assembled in a master relay unit.

Several parts of the described arrangement have been tried out and apparently worked well. However, the described assembly has never been built as a complete unit. It can be anticipated that it will work, but a few catches, which did not show in the individual parts may be still in it. The reading will evidently be linearly proportional to wax % in the above given limits of 25% - 65%. For more waxy samples it may be necessary to dilute the oil which makes continuous recording complicated. It also seems possible however, that examination of undiluted wax be done in a thinner layer e. g. 0.0500 mm or that non-linear relationship of light transmission for high wax concentrations of the usual thickness is recorded and the instrument calibrated accordingly.

It is evident that further research about crystallization and physical characteristics of paraffin waxes is a promising field. Little is known about soft paraffins and higher synthetic waxes. As seen from the commercial view point, however, such study may lead to economic methods for the isolation of paraffinic individuals, for which the future field of application as chemical intermediates etc. can presently not be fully viewed.